

THE MANNICH REACTION WITH MALONIC ACID AND FORMALDEHYDE AS A PRETREATMENT FOR MINERAL TANNAGES*

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ABSTRACT

The Mannich reaction of malonic acid and formaldehyde with animal hides and skins gives a product which has a greater affinity for metal ions. This product, when mineral-retanned, has certain properties which are improvements over those of the conventional mineral-tanned leather. These improved properties are shown to be of significance to leather-making, and the optimum conditions for carrying out this reaction have been determined.



INTRODUCTION

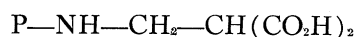
The preceding paper in this number of the *Journal* reported the results of a survey of various types of active hydrogen compounds with respect to their use in a Mannich reaction applied to hide substance. None of the active compounds evaluated showed any enhancement in tanning ability over that of formaldehyde alone. However, one of the compounds, namely malonic acid, was superior to the others in its use in a Mannich reaction as a pretreatment for chrome tanning. Since this pretreatment introduces carboxyl groups, one might expect that it would improve the binding properties of the product for metal ions. This paper reports a detailed study of the Mannich reaction between malonic acid, formaldehyde and collagen and the evaluation of the product as a substrate for mineral retannages. Tests were also conducted on whole sheepskins which were tanned in the laboratory and then processed into garment leathers by a tanner.

As was indicated in the preceding paper, the Mannich reaction with collagen is believed to involve the ϵ -amino groups of lysine and hydroxylysine residues.

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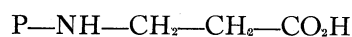
If this is the case, the reaction with formaldehyde and malonic acid would give products with structures such as I and II.



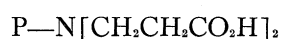
I



II



III

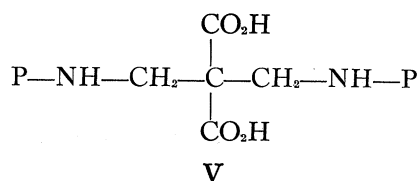


IV

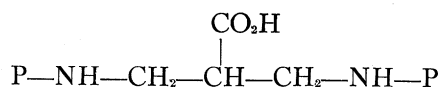
P = protein

These could undergo spontaneous decarboxylation to give products such as III and IV. At any rate, the additional carboxyl groups are undoubtedly responsible for the enhanced affinity of the product for chrome and the greater stability of the chrome-retained product (1, 2, 3).

The formation of products with structures such as V or VI, in which both active hydrogen atoms have reacted, is entirely possible. The reaction of malonic acid with formaldehyde and simple secondary amines has been shown to give products of this type (4). In collagen, this would result in crosslinking and would require the positioning of two amino groups close enough together to be



V



VI

bridged by three carbon atoms. However, there was no indication that the reaction resulted in the formation of any cross links beyond those formed in simple formaldehyde tanning, as judged from the shrinkage temperature (T_s) of the Mannich product.

Since the carboxyl groups of the collagen are also responsible for binding other metals as well as chrome, the Mannich product was also tested as a substrate for aluminum and zirconium retannages. Because of the importance of chrome in the tanning of leather, however, our major interest was in evaluating this pretreatment as a substrate for subsequent retannage with the 33 percent basic chromium sulfate used in commerce. The shrinkage temperature of the chrome-retained product was used to evaluate the effect of various factors on the pretreatment. The factors evaluated were: (1) amount of malonic acid, (2) amount of formaldehyde, (3) pH of the Mannich pretreatment, and (4) time of the Mannich pretreatment.

EXPERIMENTAL

Percentages are based on the drained, pickled weight (DPW) of the sheep-skins. Small-scale treatments and tannages were carried out in glass bottles on a tumbling machine. The formaldehyde was used in the form of a 37 percent solution in water (formalin). The percentages reported are for anhydrous formaldehyde, not for the formalin. The reagents, of reagent grade or better, were used without further purification.

Effect of Malonic Acid Concentration.—Seven pieces of pickled cabretta skins (about 40 g. each) were equilibrated individually in the pH 4 buffer system (ten percent sodium chloride, ten percent sodium formate, 200 percent float) for 30 minutes. Formaldehyde was added in the amount of five percent of the DPW, and the tumbling was continued for six hours. The following percentages of malonic acid (based on the DPW) were added, each to a different sample: 0, 1, 2, 4, 6, 8, and 10. The tumbling was continued overnight. The samples were washed and chrome-tanned in one batch using the procedure described below. The results are shown in Table I.

TABLE I
EFFECT OF AMOUNT OF MALONIC ACID
(5% Formaldehyde)

| Malonic Acid % | T _s | |
|-------------------|---------------------------------|--------------------------------|
| | Before Chrome Tanning °C. | After Chrome Tanning °C. |
| 0 | 81 | 101 |
| 1 | 80 | 104 |
| 2 | 80 | 106 |
| 4 | 80 | 109 |
| 6 | 80 | 109 |
| 8 | 79 | 110 |
| 10 | 78 | 109 |

Effect of Formaldehyde Concentration.—The above procedure was repeated on eight pieces of cabretta skins using 1, 2, 3, 4, 5, 6, 8, and 10 percent formaldehyde (based on the DPW) and a fixed amount (eight percent) of malonic acid (also based on the DPW). The chrome retanning was conducted as described below. The results are shown in Table II.

TABLE II
EFFECT OF AMOUNT OF FORMALDEHYDE
(8% Malonic Acid)

| Formaldehyde % | T _s After Chrome Tanning °C. |
|-------------------|--|
| 1 | 102 |
| 2 | 106 |
| 4 | 113 |
| 6 | 112 |
| 10 | 112 |

Effect of pH.—Three pieces of cabretta skins were equilibrated individually in the pH 4 buffer system, and one piece was equilibrated in the pH 8 buffer system (ten percent sodium sulfate, 14 percent sodium bicarbonate, 200 percent float). Adjustments were made using dilute acid or base solutions so that the pH values would be at about 3, 4, 5, and 8. The optimum amounts of formaldehyde (four percent) and malonic acid (eight percent) were added at the proper time intervals, and the rest of the procedure was the same as above. The results are shown in Table III.

TABLE III
EFFECT OF pH OF PRETREATMENT
(4% Formaldehyde, 8% Malonic Acid)

| pH | T _s After Chrome Tanning °C. |
|-----|--|
| 3.2 | 112 |
| 4.0 | 112 |
| 4.9 | 109 |
| 7.7 | 103 |

Effect of Order of Addition.—Three pieces of cabretta skins were equilibrated individually in pH 4 buffers. To one was added formaldehyde in the amount of four percent of the DPW followed by malonic acid in the amount of eight percent of the DPW two hours later. To the second, the malonic acid was added first followed by the formaldehyde two hours later. To the third, both reagents were added at the same time. The treatments were then continued as above.

Effect of Time.—Ten pieces of cabretta skins were treated with the optimum amounts of formaldehyde (four percent) and malonic acid (eight percent) at pH 4 for 2, 4, 6, 8, 16, 24, 48, 72, and 144 hours. They were then chrome-tanned according to the procedure given below. The results are shown in Table IV.

TABLE IV
EFFECT OF TIME ALLOWED FOR PRETREATMENT

(4% Formaldehyde, 8% Malonic Acid, pH ca. 4)

| Time Hr. | T _s After Chrome Tanning °C. |
|-------------|--|
| 2 | 103 |
| 4 | 107 |
| 6 | 108 |
| 8 | 109 |
| 16 | 110 |
| 24 | 112 |
| 48 | 113 |
| 72 | 116 |
| 144 | 116 |

Attempted One-Bath Treatment.—A piece of cabretta skin was pretreated with formaldehyde and malonic acid for 24 hours (pH 3.3) after which the Tanolin R,‡ in the amount of nine percent of the DPW, was added directly to the same float. The skin was then tumbled for 16 hours or longer (pH 2.7). The pH was adjusted slowly to about 4 with a dilute sodium bicarbonate solution, and the skin was washed, dried, and staked as above. The T_s, measured before drying, was 88°C.

Chrome Tanning.—Samples from the various treatments were washed and placed in a 100 percent float of a four percent sodium chloride solution. The pH of the float was adjusted to about 2.5 with a ten percent sulfuric acid solution and when it stabilized the samples were tumbled for 30 minutes. Tanolin R was added in the amount of nine percent of the DPW (in the form of either an 18 or a 36 percent solution) in three equal portions at 20 minute intervals. The samples were tumbled overnight. The pH was adjusted slowly to about 4 with a four percent sodium bicarbonate solution. When the pH remained stable, the skins were tumbled for two hours, washed, dried, and staked. The T_s (5) was measured on the wet samples immediately after washing.

The Cr₂O₃ contents of the chrome-tanned products were determined by the alkaline fusion method using a sodium thiosulfate titration, as prescribed by Official Methods of Analysis of the ALCA (6).

Aluminum Tanning.—Samples from the various treatments were washed and placed in a 100 percent float of a ten percent sodium chloride solution, and the pH of the float was adjusted to about 4 with a saturated sodium bicarbonate solution. Basic aluminum acetate was added in the amount of nine percent of the

‡Mention of brand or firm names does not constitute an endorsement by the Department of Agriculture over others of a similar nature not mentioned.

DPW in the form of an 18 percent solution. The skins were tumbled for 18 hours, and the pH was adjusted to about 4.5–5.0 with a saturated sodium bicarbonate solution, if necessary. The tumbling was continued for one hour. The skins were then washed, dried, and staked. The T_s was measured immediately after washing.

Zirconium Tanning.—Samples from the various treatments were washed and placed in a 165 percent float of a five percent sodium chloride solution, and the pH was adjusted to about 2 with a ten percent sulfuric acid solution. They were then tumbled for 30 minutes. Zircotan T was added in the amount of 25 percent of the DPW as the solid, and the tumbling was continued for three hours. Sodium acetate (dissolved in the minimum amount of water) was added in the amount of three percent of the DPW, and tumbling was continued for 20 minutes. Sodium bicarbonate (dissolved in the minimum amount of water) was added until the pH was stabilized at 4.5–5.0, and the tumbling was continued for a further 30 minutes. The skins were washed, dried, and staked. The T_s was measured before drying.

Laundering Test.—Samples ($8\frac{1}{4} \times 6\frac{3}{4}$ in.) were cut from the leather and were placed in a Maytag agitator washer to which 15 liters of water at 50°C. and 7.5 g. of Ivory soap were added. They were agitated for 15 minutes, rinsed three times, each time with 15 liters of water at 50°C. for ten minutes. The excess water was wrung from the samples by hand, and they were then laid flat to dry. The T_s was measured while the samples were still wet.

Perspiration Test.—Samples (3×3 in.) of the leather were saturated with the Roddy-Lollar artificial perspiration solution containing sodium lactate, buffered to pH 7.5, and incubated at 70°C. for 48 hours (7). The physical appearance and the T_s values after the test (8) were used to judge the results.

Preparation of Samples for Amino Acid Analysis.—Air-dried samples of the pretreated skins were ground three times in a Wiley Mill, and 0.3 g. of each was hydrolyzed by refluxing in 50 ml. of a 6*N* hydrochloric acid solution for 16 hours. The resulting solutions were evaporated to dryness on a vacuum rotary evaporator. Water (50 ml.) was added, and they were re-evaporated. The addition of water and the evaporation were repeated once more. The residue was taken up in 25 ml. of water, five g. of Norit were added, and the mixture was heated for 30 minutes on a steam bath. The solutions were filtered and evaporated as before to pale yellow oils which were diluted to 50 ml. each with a 0.1 *N* hydrochloric acid solution. The amino acid analyses were run on a Piez-Morris ion exchange column employing a continuous gradient elution buffer (9).

RESULTS AND DISCUSSION

As can be seen from the T_s of the chrome-retanned leathers (Table I), only four percent of malonic acid is needed to obtain the optimum shrink test (109–110°C.). The amount of malonic acid appears to have little effect on the T_s of the Mannich product itself, which ranged between 78 and 80°C. for varying amounts of malonic acid used in the pretreatment. In subsequent experiments, eight percent malonic acid was used to ensure the presence of an excess.

The effect of varying the amount of formaldehyde is shown in Table II. It is evident that the maximum shrinkage temperature (112–113°C.) resulted when at least four percent by weight of anhydrous formaldehyde, or about 11 percent by volume of formalin solution was used. In subsequent experiments, 11 percent of formalin (37 percent) was taken as the optimum amount.

The effect of pH on the Mannich pretreatment was investigated, and the results are summarized in Table III. The optimum shrink test after chrome-retanning (112°C.) was obtained when the pretreatment was carried out at pH in the range of 3.2–4.0. Alkaline conditions for the Mannich pretreatment gave a significantly lower T_s for the chrome-retanned product, dropping almost 10°C. when the reaction was effected at pH 7.7.

Whether the formaldehyde or the malonic acid was added first, or whether they were added at the same time, had no effect on the T_s of the final chrome-retanned product. However, the length of time allowed for the reaction of the formaldehyde and malonic acid with the skins was definitely reflected in the T_s of the chrome-retanned products. This can be seen in the data in Table IV. The maximum effect (T_s 116°C.) was obtained in three days; however, the further improvement over the effect obtained in one day (T_s 112°C.) does not warrant using the extra time.

The over-all process must be carried out in two different operations. The skin or hide must be given the pretreatment, washed free of excess reagents, and then chrome-retanned. The preferred procedure is as follows:

| | |
|--|------|
| Pickled skin or hide (DPW) | 100% |
| Sodium chloride | 10% |
| Sodium formate | 10% |
| Water | 200% |
| Tumble for 30 min. pH 4.0–4.5 | |
| Formalin (37%) | 11% |
| Malonic acid | 8% |
| Tumble overnight. pH 3.0–3.5 | |
| Wash, adjust pH to desired level for mineral tanning, and proceed with mineral tanning. | |

In order to substantiate our results and to eliminate effects due to variability within the skin, a more extensive test was designed. A pickled cabretta skin was divided into 18 roughly equal pieces, and these were grouped randomly into three lots of six pieces each. One lot was chrome-tanned with no pretreatment. These were considered the control. A second lot was pretreated with formaldehyde alone using our prescribed conditions and then retanned with chrome. The third lot was pretreated with formaldehyde and malonic acid and then retanned with chrome. The results are summarized in Table V.

TABLE V
T_s OF SKINS MINERAL-TANNED AFTER VARIOUS TREATMENTS

| Pretreatment | Mineral Tannage | Avg. T _s °C. | Spread of Values °C. |
|----------------------------------|-----------------|----------------------------|-------------------------|
| Control (none) | Chrome | 94 | 94-96 |
| Formaldehyde | Chrome | 100 | 99-101 |
| Formaldehyde and Malonic Acid | Chrome | 108 | 108-110 |
| Control (none) | Aluminum | 76 | 74-77 |
| Formaldehyde | Aluminum | 86 | 85-87 |
| Formaldehyde and Malonic Acid | Aluminum | 92 | 92-93 |
| Control (none) | Zirconium | 86 | 85-86 |
| Formaldehyde | Zirconium | 92 | 91-94 |
| Formaldehyde and Malonic Acid | Zirconium | 94 | 94 |

After chrome-tanning, the skins given no pretreatment showed the lowest T_s (94°C.), those pretanned with formaldehyde were intermediate (T_s 100°C.), and those given the Mannich pretreatment with malonic acid and formaldehyde resulted in the highest T_s, 108°C. It is quite evident that the Mannich pretreatment with malonic acid is a beneficial one.

The above test was repeated with the exception that the chrome retannage was replaced by retannage with aluminum or zirconium. As expected, the shrinkage temperatures were lower than those of the corresponding chrome-retanned products. After aluminum retannage, the T_s values were 76° for the control (no pretannage), 86°C. for the formaldehyde pretannage, and 92°C. for the pieces given the Mannich pretreatment. After zirconium retannage, the T_s values were 86, 92, and 94°C. for the control, formaldehyde pretreatment and Mannich pretreatment, respectively.

To evaluate the Mannich pretreatment further, tests were conducted on full sheepskins (cabretta, Iran and New Zealand). These were given the pretreatment with malonic acid and formaldehyde and then retanned with chrome in

the laboratory. The tanned skins were processed into garment leather with a regular pack by a tanner. As controls, a skin tanned with chrome only as well as a skin pretreated with formaldehyde alone were included for comparison. The shrinkage temperatures were measured immediately after tanning, after processing into finished leather, and after six and ten months' storage of the leathers. The results are given in Table VI. The higher initial hydrothermal stability and the increased stability with respect to aging, of the Mannich reaction products, are apparent. The leather from the pretreated skins was judged to be at least as good as the leather from the unpretreated skins.

TABLE VI
EFFECT OF PROCESSING AND AGING ON T_s OF LEATHERS

| Skin | Treatment | T_s After: | | | |
|-------------|-------------------------------|--------------------|----------------|----------------------|----------------------|
| | | Chrome Tanning °C. | Processing °C. | Aging Six Months °C. | Aging Ten Months °C. |
| Cabretta | Control | 98 | 89 | 83 | 80 |
| Cabretta | Formaldehyde | 97 | 90 | 85 | 85 |
| Cabretta | Formaldehyde and Malonic Acid | 106 | 105 | 104 | 102 |
| | Formaldehyde and Malonic Acid | | | | |
| Iran | Formaldehyde and Malonic Acid | 108 | 105 | 104 | — |
| New Zealand | Formaldehyde and Malonic Acid | 109 | 105 | 104 | — |

Samples of the above leathers resulting from the different treatments on the cabretta skins were submitted to laundering tests, and the shrinkage temperatures were measured after every other wash. These tests were carried out in hot (50°C.), soapy water. The results are given in Table VII. The value for 0

TABLE VII
EFFECT OF HOT SOAP SOLUTIONS ON THE CHROME-RETANNED LEATHERS

| Pretreatment | T_s After: | | | |
|-------------------------------|--------------|--------------|--------------|--------------|
| | 0 Washes °C. | 2 Washes °C. | 4 Washes °C. | 8 Washes °C. |
| Control (none) | 89 | 80 | 80 | 76 |
| Formaldehyde | 90 | 78 | 77 | 74 |
| Formaldehyde and Malonic Acid | 105 | 96 | 92 | 91 |

washes was the T_s immediately after finishing. In all of these cases, the fall of T_s is about the same, 14°C . However, since the shrinkage temperatures of the Mannich pretreated leathers started out so much higher, they are still in the low 90's after eight washes, while the others are in the 70's. The area stability of all of these pieces including the controls was fairly good.

The resistance of samples of the same three leathers to an artificial perspiration solution was evaluated. The shrinkage temperatures of the specimens after the test were used as a criterion of deterioration, as suggested by Bowes and Cater (8). The results are given in Table VIII. These results are difficult to interpret. There was very little improvement over the control sample but a drastic improvement over the formaldehyde pretreatment. The reasons for this are not known.

TABLE VIII
EFFECT OF AN ARTIFICIAL PERSPIRATION SOLUTION
ON THE CHROME-RETANNED LEATHERS

| Pretreatment | T_s After Test $^{\circ}\text{C}$. | Comments |
|----------------------------------|--|---|
| Control (none) | 87 | Good area stability, slightly discolored. |
| Formaldehyde | — | Too shrunken to be tested. |
| Formaldehyde and Malonic Acid | 91 | Good area stability, slightly discolored. |

Full skin tests were also performed on cabretta skins using aluminum and zirconium retannages to evaluate further the effect of the Mannich pretreatment on these. After tanning, the skins were processed into white garment leather by a tanner. The shrinkage temperatures were measured immediately after tanning, after processing, and four months after processing. The results are given in

TABLE IX
EFFECT OF PROCESSING AND AGING ON T_s OF RETANNED LEATHERS

| Pretreatment | Mineral Retannage | T_s After: | | |
|----------------------------------|----------------------|---------------------------------|------------------------------------|--|
| | | Tanning $^{\circ}\text{C}$. | Processing $^{\circ}\text{C}$. | Aging Four Months $^{\circ}\text{C}$. |
| Formaldehyde | Aluminum | 85 | 79 | 77 |
| Formaldehyde and Malonic Acid | Aluminum | 88 | 86 | 82 |
| Formaldehyde | Zirconium | 92 | 80 | 79 |
| Formaldehyde and Malonic Acid | Zirconium | 94 | 87 | 84 |

Table IX. The improvement is not as great as it was in the case of the chrome tannage, but there was a definite improvement in hydrothermal stability imparted by the Mannich pretreatment.

Samples of these leathers were submitted to the same laundering tests as were the chrome-tanned leathers. In this case, however, the tests were limited to five washes per sample. The results are given in Table X. The value for 0 washes

TABLE X
EFFECT OF HOT SOAP SOLUTIONS ON LEATHER

| Pretreatment | Mineral Retannage | T _s After: | | | |
|-------------------------------|-------------------|-----------------------|-----------------|-----------------|-----------------|
| | | 0 Washes °C. | 2 Washes °C. | 4 Washes °C. | 5 Washes °C. |
| Formaldehyde | Aluminum* | 79 | 74 | 74 | 72 |
| Formaldehyde and Malonic Acid | Aluminum* | 86 | 80 | 78 | 78 |
| Formaldehyde | Zirconium | 80 | 71 | 67 | 65 |
| Formaldehyde and Malonic Acid | Zirconium | 87 | 77 | 72 | 72 |

*These samples became stiff and discolored after only three washes.

was the T_s immediately after finishing. It is interesting to note that here too the shrinkage temperatures of the pretreated leathers and the untreated leathers fell about the same number of degrees for a given mineral retannage. In the case of the chrome retannage, it was about 14°C.; for the aluminum retannage, it was about 7°C.; and for the zirconium retannage it was 15°C. Apparently the hot soap solution is reacting in the same way with both the pretreated and the untreated leathers. However, since the Mannich pretreated leathers have a higher hydrothermal stability to begin with, they can withstand the washing more times. Samples of these leathers were submitted to the perspiration test and all failed.

In order to gain some insight into what chemical changes were taking place in the skins, a sample of the product resulting from the pretreatment with malonic acid and formaldehyde was hydrolyzed and submitted to an amino acid analysis. The same was done with a sample of a product resulting from a simple pretreatment with formaldehyde alone. Substantial losses in the amounts of lysine, hydroxylysine, and histidine were found in the hydrolyzate of the malonic acid and formaldehyde pretreated product in comparison to the amounts found in the simple formaldehyde pretreated product. In addition, the presence of several new amino acids was detected. Work is now in progress to put this on a quantitative basis and to identify the new amino acids.

SUMMARY

These studies have defined the optimum conditions for the reaction of malonic acid and formaldehyde with animal hides and skins as a pretreatment for mineral tannages. The advantages which are obtained as a result of this pretreatment have been indicated. Among these are increased chrome fixation, increased hydrothermal stability, greater resistance to aging, and increased stability to treatment with hot soap solutions. Also, some indications have been obtained pertaining to the site of the reaction in the protein.

ACKNOWLEDGMENT

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DISCUSSION

MR. MEO: Thank you, Dr. Fearheller. The leader of the discussion will be William Prentiss of Rohm and Haas Co.

DR. PRENTISS: This paper, I believe, is a testament not only to the versatility of collagen as a reaction medium, but also to what can be done with collagen in improving the properties of leather by using it as a reaction medium. For my own education, I would like to have Dr. Fearheller review the beginning of his talk when he mentioned that it was postulated that formaldehyde would undergo a Mannich-type reaction without other materials being present. Would you, Steve, discuss the differences that you get with straight formaldehyde in terms of this reaction versus the Mannich-type that you're talking about here?

DR. FEARHELLER: I spoke before of the work of Fraenkel-Conrat. He postulated that a Mannich-type reaction could take place between the amino groups

and the amido or guanidino groups of the proteins. A Mannich-type or a Mannich reaction is also possible between the amino groups of lysine residues and any tyrosine residues which are in the protein. There is only a small amount of these latter in collagen and these would have to be situated closely enough to each other in the protein for the reaction to take place.

It is known that when formaldehyde-tanned collagen is hydrolyzed, practically all of the formaldehyde can be recovered. If it was taking part in a Mannich reaction with tyrosine residues, this would not be so. You would not be able to get this back. So, the evidence is, I believe, against this type of reaction taking place.

The Mannich-type of reaction which Fraenkel-Conrat described gives cross-links between the amino groups and the amido or guanidino groups which would decompose on hydrolysis and the formaldehyde would be recovered.

DR. PRENTISS: In this discussion we have talked about a Mannich base, but there are also some interesting types of reactions which occur in subsequent tannage with corresponding improvement of properties. I have another question to ask. On your slide that showed the amount of chrome pickup with the various treatments, you noted that the malonic acid showed a greater percentage of chrome and a higher shrink temperature. Would you accomplish much the same effect if you were to put more chrome in the collagen to begin with?

DR. FAIRHELLER: You can increase the stability of the chrome-tanned product by increasing the amount of chromic oxide which you put in. You can do this in a variety of ways, one of which is increasing the amount of chromium in the tanning solution. We believe that the product that you get by doing this, would not be as stable a product as the one which we get with our pretreated material. We think that the chrome is bound more tightly by the additional carboxyl groups present in the pretreated collagen.

DR. PRENTISS: I think that an interesting observation is that this is a reaction with collagen "per se," but you worked principally with cabretta. What would you predict would happen with other types of leathers?

DR. FAIRHELLER: We picked cabretta because it is a good quality skin to start with, and it is fairly small and easy to work with. We get good penetration and also, we can react essentially all of the reactive groups in the skin. We would get the same type of reaction taking place with any skin. We might have problems getting penetration to take place with the heavier skins, but this could be overcome by using longer times.

DR. ROSS DONOVAN, Canada Packers: Other than the reaction of lysine, hydroxylysine, and histidine, is arginine not also involved in this reaction?

DR. FEAIRHELLER: We have noticed no decrease at all in the arginine.

DR. PEPPER, BLMRA: In the slide, you showed a significant drop in the shrinkage temperature on aging for ten months with all the leathers. I'm surprised to see such a drop with chrome-tanned leather. Could you tell me what the pH of the leather was? I could not imagine such a drop if the leather pH was low. I was surprised to see such a drop over ten-months natural aging in chrome-tanned leather.

DR. FEAIRHELLER: Pardon me, which sample were you referring to, Dr. Pepper?

DR. PEPPER: The chrome-tanned one which was not treated with malonic acid which you said had dropped 14 degrees or so in shrinkage temperature.

DR. PRENTISS: I think that it might be interesting to take another look at the slide involved here (Table VI). This is the illustration of the data that Dr. Pepper was talking about. There is a fairly large drop shown right there for the straight chrome-tanned material. With the malonic acid, it is quite stable over that aging period. And, isn't it right, Steve, that you have no explanation for this at this time?

DR. FEAIRHELLER: Yes.

VOICE: Would you please elaborate on the temperature conditions during the reaction? Is there an influence of temperature on the speed and the course of the reaction?

DR. FEAIRHELLER: No studies on the influence of temperature, except perhaps in one case, were done. This one was at pH 10. All the other reactions were carried out at room temperature. At pH 10, we used an elevated temperature for the reaction, about 50 to 55 degrees C. But, as far as the malonic acid pre-treatment was concerned, we made no temperature studies. We did notice that this reaction continues for a period of about three days before we get the maximum effect at room temperature. It is conceivable that if we started this out at a higher temperature, we would get complete reaction in a much shorter time.

VOICE: Would you expect any damage to the skin at a higher temperature?

DR. FEAIRHELLER: Not really. We have the formaldehyde present, and it starts tanning right away. We seem to get a formaldehyde tannage along with this addition of the carboxyl groups from the malonic acid residues. The shrink-

age temperature of the pre-treated skin is just about the same as we get with the formaldehyde-tannage under the same conditions. So we get this formaldehyde tannage right away, and I think that we could start elevating the temperature if we wanted to, at the beginning. Go up a few — well, 20 degrees or so.

VOICE: Thank you.

DR. PRENTISS: Gentlemen, we appreciate the effort that has gone into this presentation. Thank you very much, Steve.

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